

Stiffness of polymer chains

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Abstract

A formula is derived for stiffness of a polymer chain in terms of the distribution function of end-to-end vectors. This relationship is applied to calculate the stiffness of Gaussian chains (neutral and carrying electric charges at the ends), chains modeled as self-avoiding random walks, as well as semi-flexible (worm-like and Dirac) chains. The effects of persistence length and Bjerrum's length on the chain stiffness are analyzed numerically. An explicit expression is developed for the radial distribution function of a chain with the maximum stiffness.

Key-words: Elasticity (theory), Molecular networks (Theory)

1 Introduction

This paper is concerned with stiffness of polymer chains and explicit formulas for its determination. As this issue lies on the border between statistical physics of macromolecules and mechanical engineering, it has not attracted substantial attention in the past. The situation has changed dramatically in the past decade due to the development of novel experimental techniques for the direct measurements of force-extension relations on individual chains in bio-polymers. A correct measure of stiffness is important for our understanding of the differences between the responses of flexible and semi-flexible chains, as well as for the assessment of the effects of segment interactions (for example, excluded-volume interactions for neutral macromolecules and electrostatic interactions for polyelectrolyte chains) on their mechanical properties (see [1] and the references therein).

In the statistical physics of polymers, the stiffness of a macromolecule is conventionally associated with the so-called “effective spring constant:” the ratio of a force applied to a free end of a chain (its other end is assumed to be fixed) to the displacement of the free end along the force direction [2]. An advantage of this method is that the stiffness is determined in terms of the response of an individual chain, which is convenient from the experimental standpoint. A shortcoming of this approach is that it may lead to conclusions that contradict the physical intuition. As an example, we refer to the fact that this “macro”-stiffness decreases with an increase in the “micro”-stiffness characterized by the bending rigidity of a semi-flexible chain. A detailed discussion of this issue is provided in Section 2.

Mechanics of polymers focuses on the response of ensembles of macromolecules and treats an elastic modulus of an ensemble as a natural measure of its stiffness. A (shear or Young's) modulus

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is expressed in terms of the strain energy density of a polymer, and it reflects the cumulative contribution of the strain energies of chains and the energies of their interaction. When the inter-chain interactions are negligible (dilute polymer solutions) or their energy may be adequately described in a simple way (the influence of mutual interactions between chains in rubbery polymers and polymer melts is traditionally accounted for in terms of the incompressibility condition [3]), an elastic modulus of an ensemble divided by the number of chains per unit volume provides a natural measure of stiffness for an individual macromolecule.

We apply the latter approach and derive an explicit expression for the stiffness of a chain “embedded” into some ensemble subjected to affine deformations. The objective of this study is to demonstrate that the “mechanical” definition of stiffness of a macromolecule is free from the above shortcoming (an increase in the bending rigidity of a semi-flexible chain induces the growth of its stiffness, as it may be expected), on the one hand, and that it results in the same formula for the stiffness of a Gaussian chain that the conventional definition of stiffness does, on the other. To develop an analytical formula for the stiffness, we calculate the strain energy of an ensemble of chains under an arbitrary affine deformation, find the Young’s modulus at uniaxial tension, and associate the stiffness of an individual chain with its contribution into the modulus. This procedure allows an explicit expression to be derived for the stiffness of a polymer chain with an arbitrary end-to-end distribution function. The formula is illustrated by several examples, where the stiffness is expressed in terms of parameters of the distribution function, and the dependence of stiffness on these parameters is analyzed numerically.

The exposition is organized as follows. In Section 2, the conventional stiffness of a chain μ is calculated, and it is found that μ is inversely proportional to the mean square end-to-end distance of a chain. The strain energy of an ensemble of polymer chains with an arbitrary end-to-end distribution function is determined in Section 3. The formula for the strain energy is simplified for uniaxial tension with small strains in Section 4. An explicit expression for the stiffness of a chain is derived in Section 5. Section 6 focuses on several examples, where the stiffness is determined analytically, and the effect of parameters of the distribution function on this quantity is studied numerically. Some concluding remarks are formulated in Section 7.

2 Conventional stiffness of a chain

We begin with the conventional in statistical physics definition of stiffness for a polymer chain. Our aim is to develop an explicit expression for this parameter and to demonstrate that it is inversely proportional to b^{-2} , where b is the mean square end-to-end distance of the chain.

A chain is treated as a curve with some length L in a three-dimensional space. An arbitrary configuration of the chain is described by the function $\mathbf{r}(s)$, where \mathbf{r} stands for the radius vector and $s \in [0, L]$. For definiteness, we assume the end $s = 0$ to be fixed at the origin, $\mathbf{r}(0) = \mathbf{0}$, and the end $s = L$ to be free. An “internal structure” of the chain is characterized by a segment length b_0 and a number of segments $N \gg 1$, which are connected with L by the formula $L = b_0 N$.

A chain is entirely determined by its Hamiltonian $H(\mathbf{r}(s))$. Given H , the distribution of end-to-end vectors \mathbf{Q} is described by the propagator (Green’s function)

$$G(\mathbf{Q}) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}} \exp\left[-\frac{H(\mathbf{r}(s))}{k_B T}\right] \mathcal{D}[\mathbf{r}(s)], \quad (1)$$

where k_B is Boltzmann’s constant, T is the absolute temperature, and the path integral is calculated over all curves $\mathbf{r}(s)$ that start at the origin and finish at the point \mathbf{Q} ,

$$\mathbf{r}(0) = \mathbf{0}, \quad \mathbf{r}(L) = \mathbf{Q}. \quad (2)$$

The path integral in Eq. (1) is determined unambiguously by the normalization condition

$$\int G(\mathbf{Q})d\mathbf{Q} = 1. \quad (3)$$

For a chain loaded by a force \mathbf{F} at the free end, the Green function reads

$$G_F(\mathbf{Q}) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{Q}} \exp\left[-\frac{1}{k_B T} \left(H(\mathbf{r}) - \mathbf{F} \cdot \mathbf{Q}\right)\right] \mathcal{D}[\mathbf{r}(s)], \quad (4)$$

where the last term in the exponent stands for the work of external force. As this term is independent of the curve $\mathbf{r}(s)$, Eqs. (1) and (4) imply that

$$G_F(\mathbf{Q}) = G(\mathbf{Q}) \exp\left(\frac{\mathbf{F} \cdot \mathbf{Q}}{k_B T}\right). \quad (5)$$

Substitution of expression (5) into the partition function $Z_F = \int G_F(\mathbf{Q})d\mathbf{Q}$ results in

$$Z_F = \int G(\mathbf{Q}) \exp\left(\frac{\mathbf{F} \cdot \mathbf{Q}}{k_B T}\right) d\mathbf{Q}. \quad (6)$$

Differentiation of Eq. (6) with respect to \mathbf{F} implies that

$$\langle \mathbf{Q} \rangle = \frac{k_B T}{Z_F} \frac{\partial Z_F}{\partial \mathbf{F}}, \quad (7)$$

where $\langle \mathbf{Q} \rangle = \int \mathbf{Q} G_F(\mathbf{Q}) d\mathbf{Q} \left[\int G_F(\mathbf{Q}) d\mathbf{Q} \right]^{-1}$ stands for the average end-to-end vector. Formula (7) means that the vectors $\langle \mathbf{Q} \rangle$ and \mathbf{F} are collinear, while their moduli are connected by

$$\langle Q \rangle = \frac{k_B T}{Z_F} \frac{\partial Z_F}{\partial F}. \quad (8)$$

At small forces F , Eq. (8) can be linearized,

$$F = \mu \langle Q \rangle, \quad (9)$$

and the chain stiffness is described by the effective spring constant μ in Eq. (9).

To reveal a disadvantage of this definition, we consider the Marco-Siggia interpolation formula [4] for the force-stretch relation of a semi-flexible (worm-like) chain,

$$F = \frac{k_B T}{l_p} \left[\frac{1}{4} \left(1 - \frac{u}{L}\right)^{-2} - \frac{1}{4} + \frac{u}{L} \right],$$

where l_p stands for the persistence length. It follows from this equality and Eq. (9) that

$$\mu = \frac{3k_B T}{2l_p L}. \quad (10)$$

Bearing in mind that the persistence length l_p of a semi-flexible chain is connected with its bending rigidity κ by the formula $l_p = \kappa L / (k_B T)$, we find from Eq. (10) that the stiffness μ is inversely proportional to the bending rigidity κ . This conclusion appears to be counter-intuitive, because one expects that the larger the rigidity of a chain is at the micro-level (described by the parameter κ), the higher its stiffness μ is at the macro-scale [5].

To show that this shortcoming is independent of the concrete form of the force-stretch relation, we derive an explicit expression for the pre-factor μ in Eq. (9) confining ourselves to chains with isotropic Green functions $G = G_*(Q)$, where $Q = |\mathbf{Q}|$. Introducing a spherical coordinate frame $\{Q, \phi, \theta\}$ whose z vector is directed along \mathbf{F} , we find from Eq. (6) that

$$Z_F = \int_0^\infty G_*(Q) Q^2 dQ \int_0^{2\pi} d\phi \int_0^\pi \exp\left(\frac{FQ \cos \theta}{k_B T}\right) \sin \theta d\theta.$$

Calculation of the integrals over ϕ and θ results in

$$Z_F = 4\pi \frac{k_B T}{F} \int_0^\infty G_*(Q) \sinh\left(\frac{FQ}{k_B T}\right) Q dQ.$$

Substitution of this expression into Eq. (8) implies that

$$\langle Q \rangle = -\frac{k_B T}{F} + \frac{\int_0^\infty G_*(Q) \cosh\left(\frac{FQ}{k_B T}\right) Q^2 dQ}{\int_0^\infty G_*(Q) \sinh\left(\frac{FQ}{k_B T}\right) Q dQ}.$$

Setting $Q = bx$, where the mean square end-to-end distance b reads

$$b^2 = \frac{\int_0^\infty G_*(Q) Q^4 dQ}{\int_0^\infty G_*(Q) Q^2 dQ}, \quad (11)$$

and introducing the notation

$$f = \frac{Fb}{k_B T}, \quad u = \frac{\langle Q \rangle}{b}, \quad (12)$$

we arrive at the force-stretch relation

$$u = \frac{W_2(f)}{W_1(f)} - \frac{1}{f} \quad (13)$$

with

$$W_1(f) = \int_0^\infty G_*(bx) \sinh(fx) x dx, \quad W_2(f) = \int_0^\infty G_*(bx) \cosh(fx) x^2 dx.$$

At small dimensionless forces f , the hyperbolic functions are expanded into the Taylor series in f , which implies that

$$\begin{aligned} W_1(f) &= f \int_0^\infty G_*(bx) x^2 dx + \frac{f^3}{6} \int_0^\infty G_*(bx) x^4 dx + \dots, \\ W_2(f) &= \int_0^\infty G_*(bx) x^2 dx + \frac{f^2}{2} \int_0^\infty G_*(bx) x^4 dx + \dots, \end{aligned}$$

where the dots stand for terms of higher order of smallness. Substituting these expressions into Eq. (13), neglecting terms beyond the first order of smallness, returning to the initial notation, and using Eq. (11), we find that

$$f = 3u \quad (f \ll 1).$$

This equality together with Eq. (12) yields

$$F = \frac{3k_B T}{b^2} \langle Q \rangle \quad (\langle Q \rangle \ll b). \quad (14)$$

Equations (9) and (14) imply that

$$\mu = 3k_B T b^{-2}, \quad (15)$$

which means that the conventional stiffness μ of a chain with an arbitrary end-to-end distribution function is a merely geometrical parameter that is inversely proportional to the square of the average end-to-end distance b . According to Eq. (15), the stiffness of a Gaussian chain with the mean square end-to-end distance b_G reads

$$\mu_G = 3k_B T b_G^{-2}. \quad (16)$$

Obviously, Eq. (16) coincides with Eq. (10) with the persistence length $l_p = \frac{1}{2}b_0$. Setting $\Psi = \mu/\mu_G$, we find from Eqs. (15) and (16) that

$$\Psi = \left(\frac{b_G}{b}\right)^2. \quad (17)$$

3 Strain energy of a chain in an ensemble

Our aim now to derive a formula for the strain energy of a chain in an ensemble of macromolecules whose deformation at the micro-level coincides with macro-deformation (the affinity hypothesis). To simplify the analysis, we assume the deformation to be incompressible and adopt the conventional hypothesis that inter-chain interactions may be accounted for by the incompressibility condition.

Denote by \mathbf{Q} the end-to-end vector of a chain in the initial (reference) state and by \mathbf{q} the end-to-end vector in the actual (deformed) state at an arbitrary instant $t \geq 0$. The distribution functions of end-to-end vectors in the initial and deformed states read $p_0(\mathbf{Q})$ and $p(t, \mathbf{q})$, respectively. Transformation of the reference state of the chain into its deformed state is described by

$$\mathbf{q} = \mathbf{F}(t) \cdot \mathbf{Q}, \quad (18)$$

where \mathbf{F} is the deformation gradient for macro-deformation, and the dot denotes inner product. The function $\mathbf{F}(t)$ obeys the differential equation

$$\frac{d\mathbf{F}}{dt} = \mathbf{L} \cdot \mathbf{F}, \quad \mathbf{F}(0) = \mathbf{I}, \quad (19)$$

where $\mathbf{L}(t)$ is the velocity gradient, and \mathbf{I} is the unit tensor. For an incompressible macro-deformation, the Smoluchowski equation for the function $p(t, \mathbf{q})$ reads [3]

$$\frac{\partial p}{\partial t} = -\frac{\partial p}{\partial \mathbf{q}} \cdot \mathbf{L} \cdot \mathbf{q}, \quad p(0, \mathbf{q}) = p_0(\mathbf{q}). \quad (20)$$

The solution of Eq. (20) is given by

$$p(t, \mathbf{q}) = p_0(\mathbf{F}^{-1}(t) \cdot \mathbf{q}), \quad (21)$$

and it satisfies the normalization condition

$$\int p(t, \mathbf{q}) d\mathbf{q} = 1. \quad (22)$$

The distribution functions $p_0(\mathbf{Q})$ and $p(t, \mathbf{q})$ are expressed in terms of appropriate configurational free energies $U_0(\mathbf{Q})$ and $U(t, \mathbf{q})$ by the Boltzmann relations

$$p_0(\mathbf{Q}) = \exp\left[-\frac{U_0(\mathbf{Q})}{k_B T}\right], \quad p(t, \mathbf{q}) = \exp\left[-\frac{U(t, \mathbf{q})}{k_B T}\right]. \quad (23)$$

There are two ways to determine the strain energy of a chain W . According to the first, we calculate the increment ΔU of the configurational free energy caused by transition from the reference state to the actual state,

$$\Delta U(t, \mathbf{Q}) = U(t, \mathbf{Q}) - U_0(\mathbf{Q}) = -k_B T [\ln p(t, \mathbf{Q}) - \ln p_0(\mathbf{Q})],$$

and average it with the help of the distribution function in the reference state,

$$W_1(t) = -k_B T \int [\ln p(t, \mathbf{Q}) - \ln p_0(\mathbf{Q})] p_0(\mathbf{Q}) d\mathbf{Q}. \quad (24)$$

Following the other approach, the increment of the configurational free energy is calculated with respect to the actual state,

$$\Delta U(t, \mathbf{q}) = U_0(\mathbf{q}) - U(t, \mathbf{q}) = -k_B T [\ln p_0(\mathbf{q}) - \ln p(t, \mathbf{q})],$$

and it is averaged by using the distribution function in the deformed state,

$$W_2(t) = -k_B T \int [\ln p_0(\mathbf{q}) - \ln p(t, \mathbf{q})] p(t, \mathbf{q}) d\mathbf{q}. \quad (25)$$

Substitution of Eq. (21) into Eq. (24) results in

$$W_1(t) = -k_B T \int [\ln p_0(\mathbf{F}^{-1}(t) \cdot \mathbf{Q}) - \ln p_0(\mathbf{Q})] p_0(\mathbf{Q}) d\mathbf{Q}. \quad (26)$$

Combining Eqs. (21) and (25), we find that

$$W_2(t) = k_B T \int [\ln p_0(\mathbf{F}^{-1}(t) \cdot \mathbf{q}) - \ln p_0(\mathbf{q})] p_0(\mathbf{F}^{-1}(t) \cdot \mathbf{q}) d\mathbf{q}.$$

Introducing the variable \mathbf{Q} by Eq. (18) and bearing in mind that $d\mathbf{q} = d\mathbf{Q}$ for an incompressible deformation, we arrive at the formula

$$W_2(t) = k_B T \int [\ln p_0(\mathbf{Q}) - \ln p_0(\mathbf{F}(t) \cdot \mathbf{Q})] p_0(\mathbf{Q}) d\mathbf{Q}. \quad (27)$$

It seems natural to define the strain energy of a chain W as the weighted sum of the strain energies W_1 and W_2 calculated by using different ways of averaging of the configurational free energy,

$$W = (1 - a)W_1 + aW_2,$$

where $a \in [0, 1]$ is a material parameter. Substitution of Eqs. (26) and (27) into this formula implies that

$$W(t) = k_B T \int \left[a (\ln p_0(\mathbf{Q}) - \ln p_0(\mathbf{F}(t) \cdot \mathbf{Q})) + (1 - a) (\ln p_0(\mathbf{Q}) - \ln p_0(\mathbf{F}^{-1}(t) \cdot \mathbf{Q})) \right] p_0(\mathbf{Q}) d\mathbf{Q}. \quad (28)$$

For an isotropic distribution of end-to-end vectors in the reference state, we set

$$p_0(\mathbf{Q}) = P(Q^2), \quad (29)$$

where $Q^2 = \mathbf{Q} \cdot \mathbf{Q}$, and $P(r)$ is a given function of a scalar argument r . Combining Eqs. (28) and (29) and taking into account that

$$(\mathbf{F} \cdot \mathbf{Q}) \cdot (\mathbf{F} \cdot \mathbf{Q}) = \mathbf{Q} \cdot \mathbf{C} \cdot \mathbf{Q}, \quad (\mathbf{F}^{-1} \cdot \mathbf{Q}) \cdot (\mathbf{F}^{-1} \cdot \mathbf{Q}) = \mathbf{Q} \cdot \mathbf{B}^{-1} \cdot \mathbf{Q},$$

where the left and right Cauchy–Green deformation tensors read

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^\top, \quad \mathbf{C} = \mathbf{F}^\top \cdot \mathbf{F}, \quad (30)$$

and \top stands for transpose, we find that

$$W = k_B T \int \left[a \left(\ln P(Q^2) - \ln P(\mathbf{Q} \cdot \mathbf{C} \cdot \mathbf{Q}) \right) + (1-a) \left(\ln P(Q^2) - \ln P(\mathbf{Q} \cdot \mathbf{B}^{-1} \cdot \mathbf{Q}) \right) \right] P(Q^2) d\mathbf{Q}.$$

It follows from this equality and the identity

$$\int \ln P(\mathbf{Q} \cdot \mathbf{B}^{-1} \cdot \mathbf{Q}) P(Q^2) d\mathbf{Q} = \int \ln P(\mathbf{Q} \cdot \mathbf{C}^{-1} \cdot \mathbf{Q}) P(Q^2) d\mathbf{Q}$$

that the strain energy per chain reads

$$W = k_B T \int \left[a \left(\ln P(Q^2) - \ln P(\mathbf{Q} \cdot \mathbf{C} \cdot \mathbf{Q}) \right) + (1-a) \left(\ln P(Q^2) - \ln P(\mathbf{Q} \cdot \mathbf{C}^{-1} \cdot \mathbf{Q}) \right) \right] P(Q^2) d\mathbf{Q}. \quad (31)$$

Neglecting the energy of inter-chain interaction, we calculate the strain energy per unit volume of an ensemble of chains \tilde{W} as the sum of the strain energies of individual chains,

$$\tilde{W} = k_B T M \int \left[a \left(\ln P(Q^2) - \ln P(\mathbf{Q} \cdot \mathbf{C} \cdot \mathbf{Q}) \right) + (1-a) \left(\ln P(Q^2) - \ln P(\mathbf{Q} \cdot \mathbf{C}^{-1} \cdot \mathbf{Q}) \right) \right] P(Q^2) d\mathbf{Q}, \quad (32)$$

where M is the number of chains per unit volume.

4 Elastic modulus of a chain

Our aim now is to apply Eq. (32) in order to determine the elastic modulus of an ensemble of chains under uniaxial tension

$$x_1 = kX_1, \quad x_2 = k^{-\frac{1}{2}}X_2, \quad x_3 = k^{-\frac{1}{2}}X_3, \quad (33)$$

where k is an elongation ratio, $\{X_i\}$ are Cartesian coordinates in the reference state, and $\{x_i\}$ are Cartesian coordinates in the deformed state ($i = 1, 2, 3$). It follows from Eqs. (18), (30) and (33) that

$$\mathbf{C} = k^2 \mathbf{e}_1 \mathbf{e}_1 + k^{-1} (\mathbf{e}_2 \mathbf{e}_2 + \mathbf{e}_3 \mathbf{e}_3), \quad \mathbf{C}^{-1} = k^{-2} \mathbf{e}_1 \mathbf{e}_1 + k (\mathbf{e}_2 \mathbf{e}_2 + \mathbf{e}_3 \mathbf{e}_3), \quad (34)$$

where \mathbf{e}_i are base vectors of the Cartesian frame $\{X_i\}$. Substituting expressions (34) into Eq. (32) and introducing spherical coordinates $\{Q, \phi, \theta\}$, whose z axis coincides with \mathbf{e}_1 , we find that

$$\begin{aligned} \frac{\tilde{W}}{k_B T M} &= \int_0^\infty P(Q^2) Q^2 dQ \int_0^{2\pi} d\phi \int_0^\pi \left[a \left(\ln P(Q^2) - \ln P(Q^2 (k^2 \cos^2 \theta + k^{-1} \sin^2 \theta)) \right) \right. \\ &\quad \left. + (1-a) \left(\ln P(Q^2) - \ln P(Q^2 (k^{-2} \cos^2 \theta + k \sin^2 \theta)) \right) \right] \sin \theta d\theta. \end{aligned}$$

Performing integration over ϕ and introducing the new variable $x = \cos \theta$, we obtain

$$\begin{aligned} \frac{\tilde{W}}{k_B T M} &= 4\pi \int_0^\infty P(Q^2) Q^2 dQ \int_0^1 \left[a \left(\ln P(Q^2) - \ln P(Q^2 (k^2 x^2 + k^{-1} (1-x^2))) \right) \right. \\ &\quad \left. + (1-a) \left(\ln P(Q^2) - \ln P(Q^2 (k^{-2} x^2 + k (1-x^2))) \right) \right] dx. \end{aligned} \quad (35)$$

Equation (35) provides an exact formula for the strain energy density of an ensemble of chains under uniaxial tension. Simple algebra (see Appendix) implies that at small strains, when

$$k = 1 + \epsilon \quad (\epsilon \ll 1), \quad (36)$$

this equation reads

$$\frac{\tilde{W}}{k_B T M} = 4\pi\epsilon^2(K_1 + K_2), \quad (37)$$

where terms beyond the second order of smallness are disregarded, and the coefficients K_1 and K_2 are given by (the prime denotes the differentiation)

$$K_1 = - \int_0^\infty P'(Q^2) Q^4 dQ, \quad K_2 = \frac{2}{5} \int_0^\infty \left[\frac{(P'(Q^2))^2}{P(Q^2)} - P''(Q^2) \right] Q^6 dQ. \quad (38)$$

It is worth noting that the dependence of \tilde{W} on the parameter a disappears at small strains. It follows from Eq. (29) that for an isotropic Green function G ,

$$P(Q^2) = G_*(Q), \quad P'(Q^2) = \frac{G'_*(Q)}{2Q}, \quad P''(Q^2) = \frac{1}{4Q^2} \left[G''_*(Q) - \frac{G'_*(Q)}{Q} \right]. \quad (39)$$

Equations (38) and (39) imply that

$$K_1 = -\frac{1}{2} \int_0^\infty G'_*(Q) Q^3 dQ, \quad K_2 = \frac{1}{10} \int_0^\infty \frac{(G'_*(Q))^2}{G_*(Q)} Q^4 dQ - \frac{1}{10} \int_0^\infty (G''_*(Q) Q^4 - G'_*(Q) Q^3) dQ.$$

Bearing in mind that

$$\int_0^\infty G''_*(Q) Q^4 dQ = -4 \int_0^\infty G'_*(Q) Q^3 dQ,$$

we find that

$$K_2 = \frac{1}{10} \int_0^\infty \frac{(G'_*(Q))^2}{G_*(Q)} Q^4 dQ + \frac{1}{2} \int_0^\infty G'_*(Q) Q^3 dQ.$$

Substitution of these expressions into Eq. (37) results in

$$\tilde{W} = \frac{2}{5} \pi k_B T M \epsilon^2 \int_0^\infty \frac{(G'_*(Q))^2}{G_*(Q)} Q^4 dQ. \quad (40)$$

At uniaxial tension of an incompressible medium, the strain energy per unit volume \tilde{W} reads

$$\tilde{W} = \tilde{E} \epsilon^2, \quad (41)$$

where \tilde{E} denotes Young's modulus. It is worth noting that Eq. (41) does not contain the coefficient $\frac{1}{2}$ on the right-hand side that conventionally arises at small uniaxial deformations. It follows from Eqs. (40) and (41) that

$$\tilde{E} = \frac{2}{5} \pi k_B T M \int_0^\infty \frac{(G'_*(Q))^2}{G_*(Q)} Q^4 dQ. \quad (42)$$

For an ensemble of Gaussian chains with the end-to-end distribution function

$$G_*(Q) = \left(\frac{3}{2\pi b_G^2} \right)^{\frac{3}{2}} \exp\left(-\frac{3Q^2}{2b_G^2} \right), \quad (43)$$

Eq. (42) reads

$$\tilde{E}_G = \frac{18}{5b_G^4} \pi k_B T M \left(\frac{3}{2\pi b_G^2} \right)^{\frac{3}{2}} \int_0^\infty \exp\left(-\frac{3Q^2}{2b_G^2} \right) Q^6 dQ.$$

Setting $z = Q\sqrt{3}/b_G$ and calculating the integral, we find that

$$\tilde{E}_G = \frac{3}{2} k_B T M. \quad (44)$$

5 Stiffness of a polymer chain

Our aim now is to determine stiffness of a polymer chain based on Eq. (42), which coincides (to some extent) with Eq. (9). The remark in the parentheses refers to the fact that definition (9), widely used in the statistical physics of macromolecules, differs from that in mechanical engineering where the stiffness is measured as the ratio of an appropriate force to a strain (not to a displacement). To avoid this discrepancy, we replace $\langle Q \rangle$ in Eq. (9) by the ratio $\langle Q \rangle/b$, which, together with Eq. (16), implies that the conventional stiffness of a Gaussian chain is given by

$$\mu_G^0 = 3k_B T b_G^{-3}. \quad (45)$$

To obtain a counterpart of Eq. (45) grounded on Eq. (42), it seems natural to introduce a hypothetical ensemble of closely packed chains (the latter means that the number of chains per unit volume M equals v^{-1} , where $v = \frac{4}{3}\pi b^3$ is the average volume occupied by a chain), and to define the stiffness of a chain S as the Young's modulus of this ensemble. It follows from Eq. (44) that for a Gaussian chain,

$$S_G = \frac{9k_B T}{8\pi b_G^3}, \quad (46)$$

which differs from Eq. (45) by an insignificant pre-factor (of order of unity) only. In the general case, this definition implies that

$$S = \frac{3k_B T}{10b^3} \int_0^\infty \frac{(G'_*(Q))^2}{G_*(Q)} Q^4 dQ. \quad (47)$$

Excluding the coefficient b with the help of Eq. (11), we arrive at

$$S = \frac{3k_B T}{10} \int_0^\infty \frac{(G'_*(Q))^2}{G_*(Q)} Q^4 dQ \left[\frac{\int_0^\infty G_*(Q) Q^2 dQ}{\int_0^\infty G_*(Q) Q^4 dQ} \right]^{\frac{3}{2}}. \quad (48)$$

Formula (48) allows the stiffness of a chain with an arbitrary end-to-end distribution function $G_*(Q)$ to be calculated. Introducing the relative stiffness Φ as the ratio of the chain stiffness to that for a Gaussian chain, $\Phi = S/S_G$, we find from Eqs. (17), (46) and (47) that

$$\Phi = \frac{4\pi}{15} \Psi^{\frac{3}{2}} \int_0^\infty \frac{(G'_*(Q))^2}{G_*(Q)} Q^4 dQ. \quad (49)$$

6 Examples

Our purpose now is to calculate the ratio Φ for several distribution functions $G_*(Q)$ and to show that Eq. (49) leads to physically plausible dependencies of Φ on material parameters.

6.1 A flexible chain with excluded-volume interactions

The end-to-end distribution function of a flexible chain modeled as a self-avoiding random walk may be approximated by the stretched exponential function [6, 7],

$$G_*(Q) = g \exp\left[-\left(\frac{Q}{l}\right)^{2\delta}\right]. \quad (50)$$

Here δ and l are positive constants, and the pre-factor g is found from the normalization condition

$$g = \frac{1}{4\pi} \left[\int_0^\infty \exp\left(-\left(\frac{Q}{l}\right)^{2\delta}\right) Q^2 dQ \right]^{-1} = \frac{\delta}{2\pi l^3 \Gamma(\frac{3}{2\delta})},$$

where $\Gamma(x) = \int_0^\infty \exp(-z) z^{x-1} dz$ is the Euler gamma function. Substitution of expression (50) into Eq. (48) implies that

$$S = \frac{9k_B T}{40\pi l^3} (3 + 2\delta) \left[\frac{\Gamma(\frac{3}{2\delta})}{\Gamma(\frac{5}{2\delta})} \right]^{\frac{3}{2}}, \quad (51)$$

When $\delta = 1$, we set $l = b_G \sqrt{\frac{2}{3}}$ in accord with Eqs. (43) and (50). In this case, Eq. (51) is reduced to Eq. (46) for the stiffness of a Gaussian chain. It follows from Eqs. (46) and (51) that

$$\Phi = \frac{2\delta + 3}{5} \left[\frac{3\Gamma(\frac{3}{2\delta})}{2\Gamma(\frac{5}{2\delta})} \right]^{\frac{3}{2}}. \quad (52)$$

Setting $\delta \rightarrow 0$ in Eq. (52), we find that $\Phi \rightarrow 0$ due to the decay of the expression in the square brackets. Bearing in mind that

$$\lim_{\delta \rightarrow \infty} \frac{\Gamma(\frac{3}{2\delta})}{\Gamma(\frac{5}{2\delta})} = \frac{5}{3},$$

we conclude that

$$\lim_{\delta \rightarrow \infty} \frac{\Phi}{\delta} = \sqrt{\frac{5}{2}},$$

which means that Φ increases linearly with δ at sufficiently large values of the exponent. To analyze the effect of δ on the relative stiffness of a chain, we calculate Φ for $\delta \in [1, 2]$, i.e. in the interval where typical values of this parameter are located. The results of numerical simulation are presented in Figure 1, which shows that the stiffness monotonically increases (practically linearly) with δ . As δ may be treated as a measure of strength of excluded-volume interactions, this implies that repulsive segment interactions cause the growth of chain stiffness. It is worth mentioning that our conclusion contradicts Eq. (17): according to the latter formula, an increase in δ causes the growth of the average end-to-end distance b , which, in turn, induces a decrease in the conventional dimensionless stiffness Ψ .

6.2 A Gaussian chain with electric charges at the ends

Our aim now is to assess the effect of an electrostatic field on the stiffness of a Gaussian chain with two equal charges e fixed at its ends. It is assumed that the mean square end-to-end distance of the chain b_G is smaller than the Debye screening length l_D , which implies that the Coulomb interaction between charges is not screened [8]. The Hamiltonian of a non-charged Gaussian chain reads

$$H_0 = \frac{3k_B T}{2b_0} \int_0^L \left(\frac{d\mathbf{r}}{ds}(s) \right)^2 ds.$$

To account for the energy of interaction between the charges, we replace H_0 by the Hamiltonian

$$H = H_0 + \frac{e^2}{\varepsilon |\mathbf{Q}(L)|}, \quad (53)$$

where ε is the dielectric constant of an ion-free dilute solvent in which the chain is immersed. The last term on the right-hand side of Eq. (53) describes the energy of electrostatic repulsion of charges. Substituting Eq. (53) into Eq. (1) and bearing in mind that the last term is independent of the curve $\mathbf{r}(s)$, we find that

$$G(\mathbf{Q}) = g \exp\left(-\frac{3Q^2}{2b_G^2}\right) \exp\left(-\frac{l_B}{Q}\right). \quad (54)$$

The first exponent in Eq. (54) stands for the Green function for a neutral Gaussian chain, $l_B = e^2/(\epsilon k_B T)$ is the Bjerrum length, and the constant g is determined by Eq. (3),

$$g = \frac{1}{4\pi} \left(\frac{3}{b_G^2} \right)^{\frac{3}{2}} \left\{ \int_0^\infty \exp \left[- \left(\frac{z^2}{2} + \frac{\xi}{z} \right) \right] z^2 dz \right\}^{-1}$$

with $\xi = l_B \sqrt{3}/b_G$. Formula (54) correctly predicts that the probability to find the end $s = L$ of the chain in the close vicinity of the origin (the position of the other end $s = 0$) strongly decreases due to repulsion of charges. It follows from Eqs. (46), (48) and (54) that

$$\Phi(\xi) = \frac{\sqrt{3} \int_0^\infty \exp(-\frac{z^2}{2} - \frac{\xi}{z}) (z^3 - \xi)^2 dz}{5 \int_0^\infty \exp(-\frac{z^2}{2} - \frac{\xi}{z}) z^2 dz} \left[\frac{\int_0^\infty \exp(-\frac{z^2}{2} - \frac{\xi}{z}) z^2 dz}{\int_0^\infty \exp(-\frac{z^2}{2} - \frac{\xi}{z}) z^4 dz} \right]^{\frac{3}{2}}. \quad (55)$$

The function $\Phi(\xi)$ is plotted (in the double logarithmic coordinates with $\log = \log_{10}$) in Figure 2. According to this figure, Φ decreases with ξ . At sufficiently large ξ , the curve $\Phi(\xi)$ may be approximated by the dependence

$$\log \Phi = \Phi_0 - \Phi_1 \log \xi, \quad (56)$$

where the coefficients Φ_0 and Φ_1 are determined by the least-squares method. Our results of numerical analysis demonstrate that $\Phi_1 \approx \frac{1}{3}$, which implies the scaling law

$$\Phi \propto \left(\frac{b_G}{l_B} \right)^{\frac{1}{3}} \quad (l_B \gg b_G). \quad (57)$$

The conclusion that the stiffness of a charged Gaussian chain is smaller than that of an appropriate neutral chain may be explained by the fact that electrostatic repulsion of chain ends increases the end-to-end distance in the reference state, which means that the number of available configurations, and, as a consequence, the chain entropy are reduced. It is worth noting, however, that the same explanation is inapplicable to flexible chains with excluded-volume interactions, because Eq. (52) demonstrates the growth of stiffness due to segment interactions.

6.3 A flexible chain with the maximum stiffness

It is of interest to determine the distribution function of end-to-end vectors for a chain whose stiffness is maximal. The analysis is confined to smooth radial distribution functions $G_*(Q)$, which are positive at any $Q \in [0, \infty)$, tend to zero rather rapidly as $Q \rightarrow \infty$, and remain bounded together with their derivatives in the vicinity of $Q = 0$. We suppose also that the second moment of the distribution function $\langle Q^2 \rangle = b_c^2$ and the most probable end-to-end distance l_c are fixed. The latter quantity is determined from the condition of maximum of the function $G_*(Q)Q^2$,

$$l_c = \arg \max_Q G_*(Q)Q^2.$$

To demonstrate that these conditions uniquely determine the radial distribution function of a chain with the maximum stiffness, we present Eq. (47) in the form

$$S = \frac{3k_B T}{40\pi b_c^3} \mathcal{F}(G_*(Q)), \quad (58)$$

where the functional \mathcal{F} reads

$$\mathcal{F}(y(Q)) = \int_0^\infty \frac{(y'(Q))^2}{y(Q)} Q^4 dQ \left[\int_0^\infty y(Q) Q^2 dQ \right]^{-1}. \quad (59)$$

The presence of the last term in Eq. (59) allows arbitrary (non-normalized) Green functions $y(Q)$ to be considered. Denote by λ the maximum of the functional $\mathcal{F}(y)$ on the set of smooth positive functions $y(Q)$. A function $y_0(Q)$ that maximizes $\mathcal{F}(y)$ satisfies the equality

$$\int_0^\infty \left[\frac{(y'_0(Q))^2 Q^4}{y_0(Q)} - \lambda y_0(Q) Q^2 \right] dQ = 0. \quad (60)$$

The first term in Eq. (60) is transformed by integration by parts

$$\int_0^\infty \frac{(y'_0(Q))^2 Q^4}{y_0(Q)} dQ = \int_0^\infty \frac{y'_0(Q) Q^4}{y_0(Q)} dy_0(Q) = y'_0(Q) Q^4 \Big|_0^\infty - \int_0^\infty y_0(Q) \left(\frac{y'_0(Q) Q^4}{y_0(Q)} \right)' dQ.$$

Our assumptions regarding the properties of the function $y_0(Q)$ imply that the out-of-integral term vanishes. Combining this equality with Eq. (60), we obtain

$$\int_0^\infty \left[\left(\frac{y'_0(Q) Q^4}{y_0(Q)} \right)' + \lambda Q^2 \right] y_0(Q) dQ = 0.$$

This equation is fulfilled provided that the function $y_0(Q)$ obeys the differential equation

$$\left(\frac{y'_0(Q) Q^4}{y_0(Q)} \right)' + \lambda Q^2 = 0. \quad (61)$$

Integration of Eq. (61) implies that

$$\frac{y'_0(Q)}{y_0(Q)} = \frac{B}{Q^4} - \frac{\lambda}{3Q}, \quad (62)$$

where B is an arbitrary constant. The general solution of Eq. (62) reads

$$y_0(Q) = A Q^{-\frac{\lambda}{3}} \exp\left(-\frac{B}{3Q^3}\right), \quad (63)$$

where A is another constant. The parameters A , B and λ are found from the equalities

$$4\pi \int_0^\infty y_0(Q) Q^2 dQ = 1, \quad 4\pi \int_0^\infty y_0(Q) Q^4 dQ = b_c^2, \quad [y_0(Q) Q^2]'_{Q=l_c} = 0, \quad (64)$$

which describe the normalization condition for the distribution function, the definition of the mean square end-to-end distance, and the definition of the most probable end-to-end distance, respectively. Substitution of Eq. (63) into the last formula in Eq. (64) results in

$$B = \frac{\lambda - 6}{3} l_c^3. \quad (65)$$

Dividing the second equality in Eq. (64) by the first and using Eqs. (63) and (65), we find that

$$b_c^2 = \frac{\int_0^\infty \exp\left(-\frac{(\lambda-6)l_c^3}{9Q^3}\right) Q^{-\frac{\lambda-12}{3}} dQ}{\int_0^\infty \exp\left(-\frac{(\lambda-6)l_c^3}{9Q^3}\right) Q^{-\frac{\lambda-6}{3}} dQ}.$$

Setting $z = Q/l_c$ and calculating the integrals, we arrive at the formula

$$\left(\frac{b_c}{l_c} \right)^2 = \left(\frac{\lambda - 6}{9} \right)^{\frac{2}{3}} \frac{\Gamma(\frac{\lambda-15}{9})}{\Gamma(\frac{\lambda-9}{9})}. \quad (66)$$

For a Gaussian chain with $b_c = b_G$ and $l_c = b_G\sqrt{\frac{2}{3}}$, we set $\lambda = 9\lambda_1$ and find that λ_1 obeys the transcendental equation

$$\left(\lambda_1 - \frac{2}{3}\right)^{\frac{2}{3}} \frac{\Gamma(\lambda_1 - \frac{5}{3})}{\Gamma(\lambda_1 - 1)} = \frac{3}{2}. \quad (67)$$

It follows from Eqs. (46) and (58) that

$$\frac{S_G}{S_{\max}} = \frac{5}{27\lambda_1}. \quad (68)$$

Solving Eq. (67) for λ_1 numerically and using Eq. (68), we obtain $\lambda_1 = 3.1809$ and $S_G = 0.0582 S_{\max}$. The result is rather surprising. It means that Gaussian chains are not so flexible: the stiffness of a Gaussian chain is about 6% of the maximal stiffness of a chain with the same geometrical parameters.

The difference between the shapes of the radial distribution functions for a Gaussian chain and for a chain with the maximum stiffness is seen in Figure 3, where the results of numerical simulation are presented for $b_G = 1.0$. The shape of a Gaussian chain is described by Eq. (43), whereas the shape of a chain with the maximum stiffness is determined by Eq. (63), where B is given by Eq. (65), λ is calculated from Eq. (67), and A is found from Eq. (3). Figure 3 demonstrates that the distribution function of end-to-end vectors for a chain with the maximum stiffness vanishes in the vicinity of the point $Q = 0$, has a pronounced maximum at $Q = l_c$, and slowly decreases with Q when $Q > l_c$.

It is worth noting the importance of the assumption regarding the smoothness of the distribution function $G_*(Q)$ and its positiveness in $[0, \infty)$. If these constraints are violated, a distribution function of end-to-end vectors may be constructed for a chain with an infinite stiffness. An example is given by

$$G_*(Q) = \frac{3}{8\pi l} \left[1 - \left(\frac{Q}{l}\right)^2\right] \quad (Q \leq l), \quad G_*(Q) = 0 \quad (Q > l). \quad (69)$$

Formula (69) and similar expressions for the radial distribution function naturally arise for polymer chains treated as random walks governed by equations of anomalous diffusion [9, 10]. It should be emphasized, however, that Eq. (47) is inapplicable to chains, whose distribution functions have finite supports. This is explained by the fact that Eq. (47) is grounded on the hypothesis regarding an affine deformation of a network, while the probability $p(t, \mathbf{q})$ is not defined by Eq. (20), when the vector $\mathbf{q} = \mathbf{F} \cdot \mathbf{Q}$ is located in the domain where the distribution function $p_0(\mathbf{Q})$ vanishes.

6.4 A semi-flexible chain

Semi-flexible chains provide another class of macromolecules, for which the applicability of Eqs. (47) and (48) may be questioned. This is explained by the fact that the integral in Eq. (32) for the strain energy density diverges. On the other hand, appropriate integrals in Eq. (48) converge, and it is tempting to employ this formula in order to calculate the stiffness. Our aim now is to assess the effect of persistence length l_p on the stiffness of worm-like chains and to demonstrate that Eq. (48) results in a physically plausible behavior of the function $S(l_p)$.

Assuming that $G_*(Q) = \Lambda(Q/L)$, where L stands for the chain length, and setting $z = Q/L$, we find from Eq. (48) that

$$S = \frac{3k_B T}{10} \int_0^\infty \frac{(\Lambda(z))^2}{\Lambda(z)} z^4 dz \left[\frac{\int_0^\infty \Lambda(z) z^2 dz}{\int_0^\infty \Lambda(z) z^4 dz} \right]^{\frac{3}{2}}. \quad (70)$$

We begin with the analysis of semi-flexible chains with the distribution function [11]

$$\begin{aligned}\Lambda(z) &= \frac{g}{[\zeta(1-z)]^{\frac{3}{2}}} \sum_{m=1}^{\infty} \exp\left[-\left(\frac{m-\frac{1}{2}}{(\zeta(1-z))^{\frac{1}{2}}}\right)^2\right] H_2\left(\frac{m-\frac{1}{2}}{(\zeta(1-z))^{\frac{1}{2}}}\right) \quad (z < 1), \\ \Lambda(z) &= 0 \quad (z \geq 1).\end{aligned}\tag{71}$$

Here $\zeta = l_p/L$ stands for the dimensionless persistence length, $H_2(z) = 4z^2 - 2$, and the pre-factor g is determined by Eq. (3). We substitute expression (71) into Eq. (70), calculate the integrals numerically (by the Simpson method with the step $\Delta z = 0.001$) taking into account 500 terms in the series, and calculate S . The ratio $\overline{S} = S/(k_B T)$ is plotted versus ζ in Figure 4 at relatively small values of ζ (in the linear scale) and in Figure 5 at arbitrary ζ (in the double logarithmic scale).

The results of numerical simulation based on Eq. (71) are compared with those found by using the radial distribution functions proposed in [12, 13],

$$\Lambda(z) = \frac{g}{(1-z^2)^{\frac{9}{2}}} \exp\left[-\frac{9}{8\zeta(1-z^2)}\right] \quad (z < 1),\tag{72}$$

$$\Lambda(z) = \frac{g}{(1-z^2)^{\frac{3}{2}}(2-z^2)^3} \exp\left[-\frac{3}{4\zeta(1-z^2)}\right] \quad (z < 1).\tag{73}$$

Equations (72) and (73) presume the function $\Lambda(z)$ to vanish at $z \geq 1$, in accord with the second equality in Eq. (71). The ratios \overline{S} calculated from Eqs. (70), (72) and (73) are plotted versus the dimensionless persistence length ζ in Figure 5. The results of numerical analysis are approximated by the function

$$\log \overline{S} = S_0 + S_1 \log \zeta,\tag{74}$$

where the coefficients S_0 and S_1 are determined by the least-squares technique. Figure 5 shows that Eq. (74) correctly fits the dependence $S(\zeta)$ at relatively large values of ζ . The coefficient S_1 in Eq. (74) is close to two for all models under investigation, which implies that the stiffness of a worm-like chain grows with persistence length l_p being proportional to l_p^2 (in other words, being proportional to the square of the bending stiffness κ), as it is expected [5]. However, some discrepancies between the scaling prediction

$$S \propto l_p^\alpha\tag{75}$$

with $\alpha = 2$ and the numerical results should be mentioned. The exponent α practically equals 2 for distribution function (72), and it is close to $\frac{9}{5}$ for functions (71) and (73) (no changes in α are observed with the growth of the number of terms in the series and a decrease in the step Δz employed in numerical integration). The deviations of the exponent for the distribution functions (71) and (73) from $\alpha = 2$ may be explained by the fact that inadequate approximations of the Green function were chosen in the derivation of these relations. The method suggested in [11] is based on the hypothesis that any curve $\mathbf{r}(s)$ in Eq. (1) is close enough to the straight line connecting the points $\mathbf{r}(0) = \mathbf{0}$ and $\mathbf{r}(L) = \mathbf{Q}$. This assumption is correct for end-to-end vectors \mathbf{Q} with $Q = L$, but it may cause large discrepancies at $Q < L$ driven by the constraint on the curve length. Figure 5 reveals that the method of softening this constraint proposed in [12] (the local restriction on the length of the tangent vector is replaced by the global one) leads to a substantially better approximation, whereas the approach developed in [13] does not improve substantially the quality of approximation.

Based on another way of thinking, the so-called Dirac chains were introduced in [14] with the radial distribution function

$$\Lambda(z) = \frac{g}{\sqrt{1-z^2}} I_1\left(\frac{3\sqrt{1-z^2}}{2\zeta}\right) \quad (z < 1), \quad \Lambda(z) = 0 \quad (z \geq 1). \quad (76)$$

Here ζ is the dimensionless persistence length,

$$I_1(z) = \frac{2}{z} \sum_{m=1}^{\infty} \frac{m(\frac{1}{4}z^2)^m}{(m!)^2}$$

is the modified Bessel function, and the pre-factor g is determined by Eq. (3). To assess the stiffness of a chain with the distribution function (76), we substitute this expression into Eq. (70), calculate the stiffness S , and plot the ratio \bar{S} versus ζ in Figure 6 together with its approximation by Eq. (74). This figure shows that at relatively small persistence lengths, $l_p < 0.3L$, the stiffness S increases with l_p , but the scaling exponent $\alpha \approx 1.5$ is lower than that for Eqs. (71) to (73). With a further increase in the persistence length l_p , the stiffness diminishes, which indicates that the model becomes inappropriate at relatively large values of l_p .

7 Concluding remarks

A “mechanical” definition of stiffness is introduced for a polymer chain, and an explicit formula is derived to express the stiffness in terms of the radial distribution function. According to our approach, a polymer chain is “embedded” into an affine ensemble, and the stiffness is defined as an elastic modulus per chain of the ensemble.

This relation is applied to calculate the stiffness of (i) a Gaussian chain, (ii) a flexible chain modeled as a self-avoiding random walk, and (iii) a Gaussian chain carrying electric charges at its ends. The influence of the Bjerrum length l_B on the stiffness S of a charged Gaussian chain has been studied numerically. It is revealed that S decreases with l_B being proportional to $l_B^{-\frac{1}{3}}$.

An analytical formula is derived for the distribution function of a chain with the maximum stiffness. It is found that the stiffness of a Gaussian chain is about 6% of that for a chain with the maximum stiffness and the same geometrical parameters.

The effect of persistence length l_p on the stiffness of semi-flexible chains has been evaluated numerically. It is demonstrated that the stiffness of worm-like chains increases with l_p following the pattern $E \propto l_p^\alpha$ with $\alpha \approx 2$. For a Dirac chain, stiffness increases with persistence length when l_p is less than 30% of the contour length L , and the scaling exponent α is close to $\frac{3}{2}$.

Appendix

Neglecting terms beyond the second order of smallness with respect to ϵ , we find from Eq. (36) that

$$\begin{aligned} k^2 x^2 + k^{-1}(1-x^2) &= 1 - \epsilon(1-3x^2) + \epsilon^2, \\ k^{-2} x^2 + k(1-x^2) &= 1 + \epsilon(1-3x^2) + 3\epsilon^2 x^2. \end{aligned} \quad (A-1)$$

The expansion of the function $\ln P(Q^2(1+\alpha))$ in a Taylor series with respect to α in the vicinity of the point $\alpha = 0$ reads

$$\ln P(Q^2(1+\alpha)) = \ln P(Q^2) + \alpha Q^2 \frac{P'(Q^2)}{P(Q^2)} + \frac{1}{2} \alpha^2 Q^4 \frac{P''(Q^2)P(Q^2) - (P'(Q^2))^2}{P^2(Q^2)} + \dots, \quad (A-2)$$

where the prime stands for the derivative of the function P . It follows from Eqs. (A-1) and (A-2) that

$$\begin{aligned}\ln P(Q^2) - \ln P(Q^2(k^2x^2 + k^{-1}(1-x^2))) &= \epsilon Q^2(1-3x^2) \frac{P'(Q^2)}{P(Q^2)} - \epsilon^2 Q^2 \frac{P'(Q^2)}{P(Q^2)} \\ &\quad + \frac{1}{2} \epsilon^2 Q^4 (1-3x^2)^2 \frac{(P'(Q^2))^2 - P''(Q^2)P(Q^2)}{P^2(Q^2)}, \\ \ln P(Q^2) - \ln P(Q^2(k^{-2}x^2 + k(1-x^2))) &= -\epsilon Q^2(1-3x^2) \frac{P'(Q^2)}{P(Q^2)} - 3\epsilon^2 Q^2 x^2 \frac{P'(Q^2)}{P(Q^2)} \\ &\quad + \frac{1}{2} \epsilon^2 Q^4 (1-3x^2)^2 \frac{(P'(Q^2))^2 - P''(Q^2)P(Q^2)}{P^2(Q^2)}.\end{aligned}$$

Integrating these expressions with respect to x and taking into account that

$$\int_0^1 (1-3x^2)dx = 0, \quad \int_0^1 3x^2dx = 1, \quad \int_0^1 (1-3x^2)^2dx = \frac{4}{5},$$

we find that

$$\begin{aligned}&\int_0^1 [\ln P(Q^2) - \ln P(Q^2(k^2x^2 + k^{-1}(1-x^2)))] dx \\ &= \int_0^1 [\ln P(Q^2) - \ln P(Q^2(k^{-2}x^2 + k(1-x^2)))] dx \\ &= \epsilon^2 \left[-\frac{P'(Q^2)}{P(Q^2)} Q^2 + \frac{2}{5} \frac{(P'(Q^2))^2 - P''(Q^2)P(Q^2)}{P^2(Q^2)} Q^4 \right].\end{aligned}\tag{A-3}$$

Equations (37) and (38) follow from Eqs. (35) and (A-3).

References

- [1] Cocco S, Marco JF, Monasson R, Sarkar A and Yan J, Force-estension behavior of folding polymers, 2003 Eur. Phys. J. E 10 249
- [2] de Gennes PG, Scaling Concepts in Polymer Physics, 1979 (Ithaca, NY: Cornell Univ. Press)
- [3] Doi M and Edwards SF, The Theory of Polymer Dynamics, 1986 (Oxford: Clarendon Press)
- [4] Marko JF and Siggia ED, Stretching DNA, 1995 Macromolecules 28 8759
- [5] MacKintosh FC, Käs J and Janmey PA, Elasticity of semiflexible biopolymer networks, 1995 Phys. Rev. Lett. 75 4425
- [6] McKenzie DS and Moore MA, Shape of a self-avoiding walker or polymer chain, 1971 J. Phys. A 4 L82
- [7] des Cloizeaux J, Lagrangian theory for a self-avoiding random chain, 1974 Phys. Rev. A 10 1665
- [8] Zandi R, Rudnick J and Golestanian R, Probing polyelectrolyte elasticity using radial distribution function, 2003 Phys. Rev. E 67 021803
- [9] Malacarne LC, Mendes RS, Pedron IT and Lenzi EK, Nonlinear equation for anomalous diffusion: unified power-law and stretched exponential exact solution, 2001 Phys. Rev. E 63 030101(R)
- [10] Pedron IT, Mendes RS, Malacarne LC and Lenzi EK, Nonlinear anomalous diffusion equation and fractal dimension: exact generalized Gaussian solution, 2002 Phys. Rev. E 65 041108
- [11] Wilhelm J and Frey E, Radial distribution function of semiflexible polymers, 1996 Phys. Rev. Lett. 77 2581
- [12] Ha B-Y and Thirumalai D, Semiflexible chains under tension, 1997 J. Chem. Phys. 106 4243
- [13] Winkler RG, Deformation of semiflexible chains, 2003 J. Chem. Phys. 118 2991
- [14] Kholodenko A and Vilgis T, Elastic response of the Dirac chain, 1994 Phys. Rev. E 50 1257

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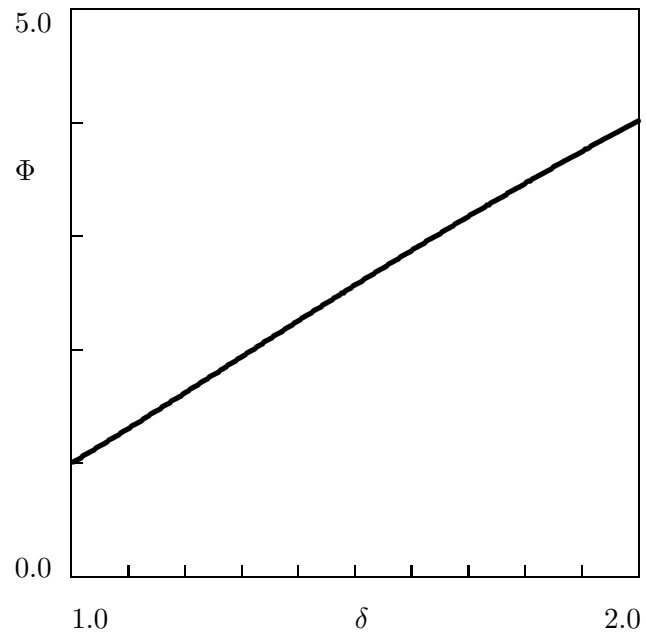


Figure 1:

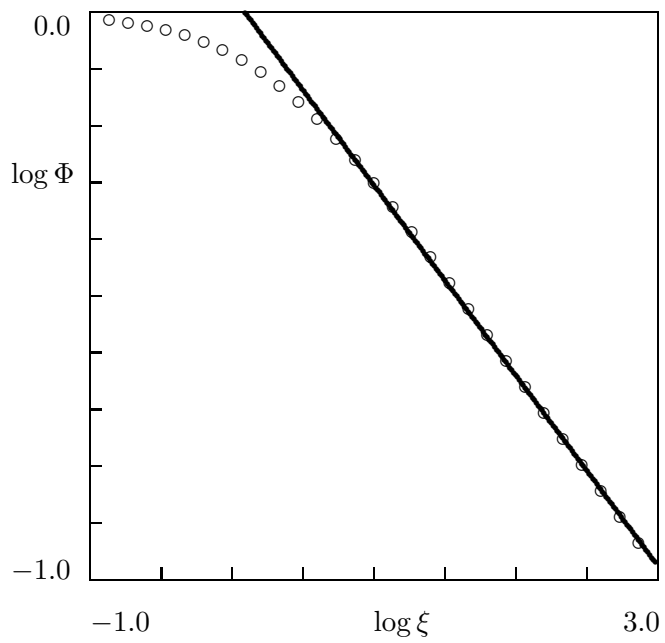


Figure 2:

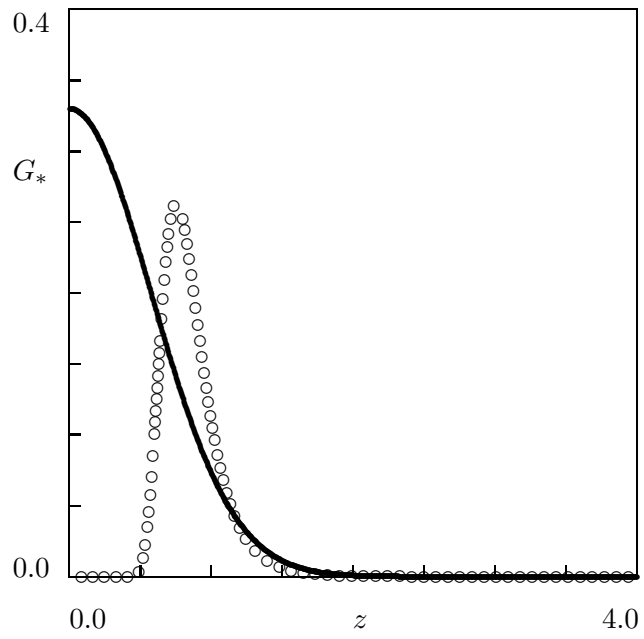


Figure 3:

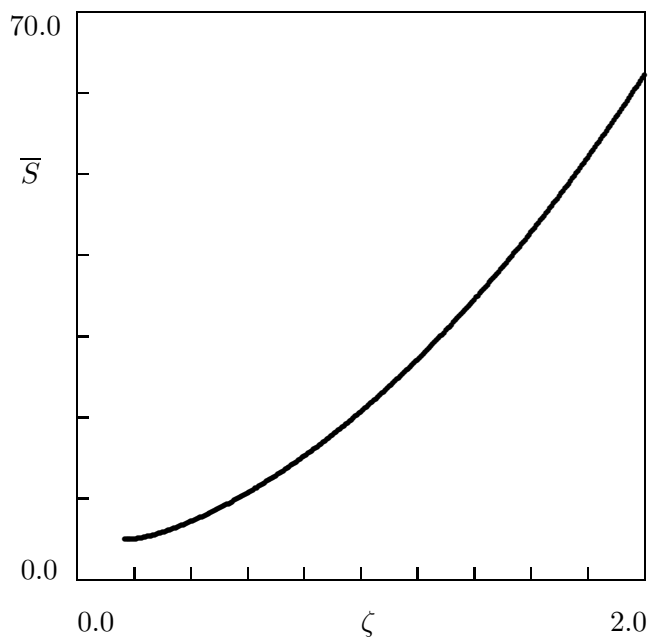


Figure 4:

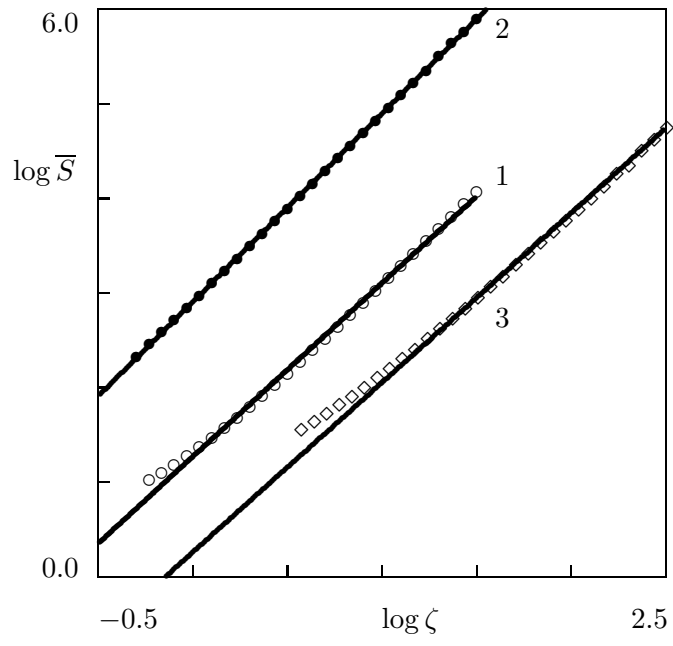


Figure 5:

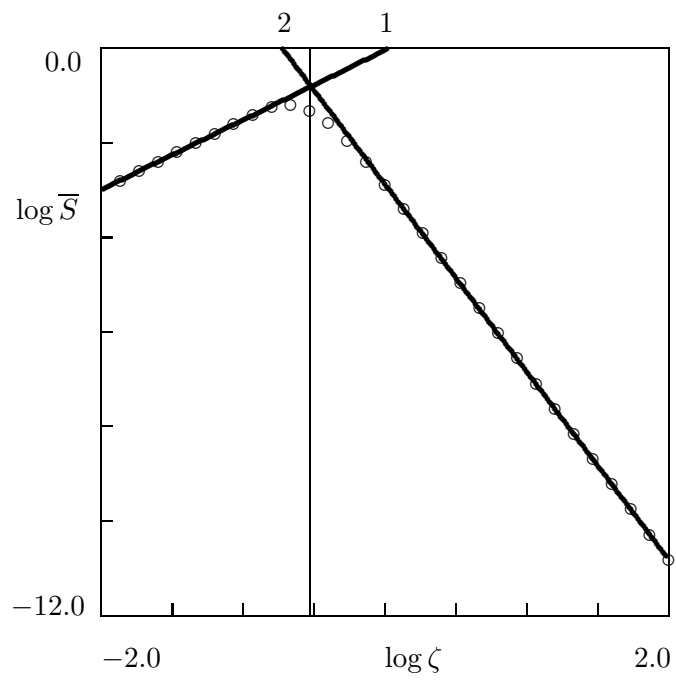


Figure 6: